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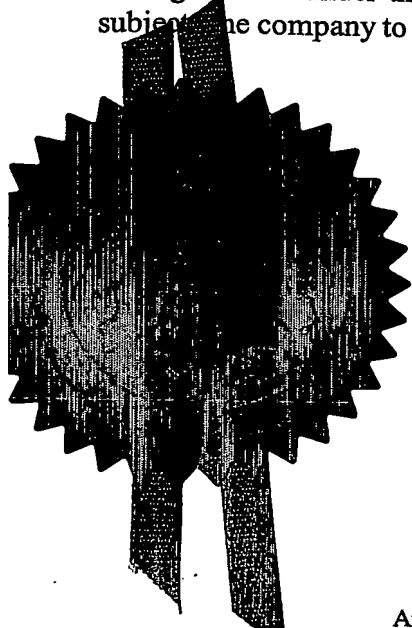
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Dated 9 February 2005

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# request for grant of a patent

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Your reference

SMC 60650/GB/P1

Patent application number

(The Patent Office will fill in this part)

0407852.3

Full name, address and postcode of the or of  
each applicant (underline all surnames)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS

Patents ADP number (if you know it)

07764137001

If the applicant is a corporate body, give the  
country/state of its incorporation

GB

Title of the invention

Improvements in and relating to organic  
semi-conducting layers

5. Name of your agent (if you have one)

PARLETT, Peter Michael

"Address for service" in the United Kingdom  
to which all correspondence should be sent  
(including the postcode)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS  
United Kingdom

Patents ADP number (if you know it)

6. If you are declaring priority from one or more  
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8. Is a statement of inventorship and of right  
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Yes

- a) any applicant named in part 3 is not an inventor, or
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Description

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Claim(s)

Abstract

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

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Request for substantive examination (Patents Form 10/77)

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11.

I/We request the grant of a patent on the basis of this application.

Signature

G Shepherd Date 7/4/04

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K M Pinder/Mrs G Shepherd 0161 721 1361/2

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SMC 69659  
04 12 2007

APPLICANTS

Avecia Limited.

TITLE

IMPROVEMENTS IN AND RELATING TO ORGANIC SEMICONDUCTING LAYERS

## IMPROVEMENTS IN AND RELATING TO ORGANIC SEMICONDUCTING LAYERS

The present invention relates to an organic semiconducting layer formulation, a layer comprising the same, a process for preparing the formulation and layer and electronic devices (including OFETs) comprising the same.

In recent years, there has been development of organic semiconducting materials in order to produce more versatile, lower cost electronic devices. Such materials find application in a wide range of devices or apparatus, including in organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), photodetectors, photovoltaic (PV) cells, sensors, memory elements, logic circuits and as organic photoconductors (OPCs) in electrophotographic devices, to name just a few. The organic semiconducting materials are typically present in the electronic device in the form of a thin layer, e.g. less than 1 micron thick.

Pentacene has shown promise as an organic semiconducting material. Pentacene though has been described as requiring a highly crystalline structure in order to provide a molecular orientation which results in good charge mobility. Thus, pentacene thin films have been vapour deposited in the prior art (pentacene is also rather insoluble in common solvents). However, vapour deposition requires expensive and sophisticated equipment. In view of the latter problem, another approach has been to apply a solution containing a precursor pentacene and then chemically converting, e.g. by heat, the precursor compound into pentacene. However, the latter method is also complex and it is difficult to control in order to obtain the necessary ordered structure for good charge mobility.

Soluble pentacene compounds have recently been described in the prior art as organic semiconducting compounds, see for example US 2003/0116766 A (Takahashi) and US 6,690,029 (Anthony) and their use in FETs has been suggested in WO 03/016599 (Asahi). In the latter reference, a solution of the soluble pentacene was deposited on a substrate and the solvent evaporated to form a thin film of the pentacene. However, the soluble pentacenes have been described in US 6,690,029 and WO 03/016599 as still requiring a highly crystalline structure in the thin film for acceptable charge mobility, especially when used in FETs, which means that the pentacenes must still be carefully deposited. Thus, the prior art is careful not to dilute the pentacene in any way, otherwise it would be expected to disrupt the crystalline structure of the pentacene and hence reduce charge mobility.

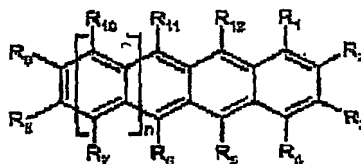
Improved charge mobility is one goal of new electronic devices. Another goal is the stability and integrity of the organic semiconductor layer. A way potentially to improve organic semiconductor layer stability and integrity in devices would be to include the organic semiconducting component in an organic binder resin. However, whenever an

organic semiconducting component is combined with a binder it is effectively "diluted" by the binder and a reduction of charge mobility is to be expected. Among other things, diluting an organic semiconductor by mixing with binders disrupts the molecular order in the semiconducting layer. Diluting an organic semiconducting component in the channel of an OFET for example is particularly problematic as any disruption of the orbital overlap between molecules in the immediate vicinity of the gate insulator (the first few molecular layers) is expected to reduce mobility. Electrons or holes then are forced to extend their path into the bulk of the organic semiconductor, which is undesirable. Certain organic semiconducting materials are expected to be more susceptible than others to the effects of use in a binder. Since pentacenes have been taught as requiring highly ordered structures for useful charge mobility, it has not previously been considered desirable to include pentacenes with binders. In WO 03/030278 (Philips) it was attempted to use binders but there it was shown that a gradual reduction of FET mobility occurs when a (precursor) pentacene is mixed with increasing amounts of binder, even with amounts less than 5% binder.

Certain low polarity binder resins are described in WO 02/45184 (Avecia) for use with organic semiconductors in FETs. However, a reduction in charge mobility is still expected when the semiconductor is diluted in the binder.

Among the objects of the present invention is to reduce or overcome the disadvantages in organic semiconducting layers described above.

According to the present invention there is provided an organic semiconducting layer formulation, which layer formulation comprises an organic binder resin and a polyacene compound of formula A:



Formula A

wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$ , which may be the same or different, independently represents hydrogen; an optionally substituted  $C_1$ - $C_{40}$  carbonyl or hydrocarbonyl group; an optionally substituted  $C_1$ - $C_{40}$  alkoxy group; an optionally substituted  $C_6$ - $C_{40}$  aryloxy group; an optionally substituted  $C_7$ - $C_{40}$  alkylaryloxy group; an optionally substituted  $C_2$ - $C_{40}$  alkoxy carbonyl group; an optionally substituted  $C_7$ - $C_{40}$  aryloxy carbonyl group; a cyano group ( $-CN$ ); a carbamoyl group ( $-C(=O)NH_2$ ); a haloformyl group ( $-C(=O)-X$ , wherein  $X$  represents a halogen atom); a formyl group ( $-C(=O)-H$ ); an isocyano group; an isocyanate group; a thiocyanate group or a

thiocyanate group; an optionally substituted amino group; a hydroxy group; a halo group; or an optionally substituted silyl group;

wherein each pair of  $R_2$  and  $R_3$  and/or  $R_8$  and  $R_9$  may be cross-bridged to form a  $C_4$ - $C_{10}$  saturated or unsaturated ring, which saturated or unsaturated ring may be intervened by an oxygen atom, a sulphur atom or a group shown by formula:  $-N(R_a)-$  (wherein  $R_a$  is a hydrogen atom or an optionally substituted hydrocarbon group), or may optionally be substituted;

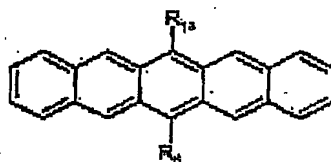
wherein one or more of the carbon atoms of the polyacene skeleton may optionally be substituted by a heteroatom selected from N, P, As, O, S, Se and Te; and

wherein any two or more of the substituents  $R_1$ - $R_{12}$  which are located on adjacent ring positions of the polyacene may, together, optionally constitute a further aromatic ring system fused to the polyacene.

Preferably,  $n=2$ , i.e. the polyacene compound is a pentacene compound.

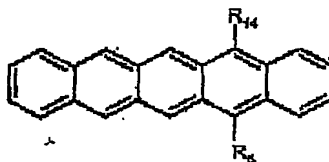
More preferably, the pentacene compound is a compound selected from any one of Compound Groups 1 to 7 wherein:

Compound Group 1 is represented by formula 1:



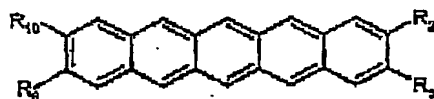
Formula 1

Compound Group 1 is represented by formula 2:



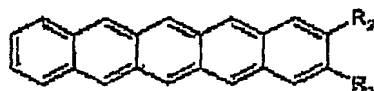
Formula 2

Compound Group 1 is represented by formula 3:



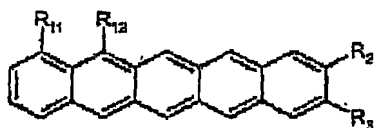
Formula 3

Compound Group 4 is represented by formula 4:



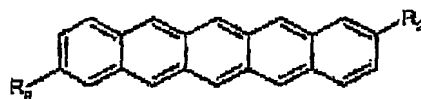
Formula 4

Compound Group 5 is represented by formula 5:



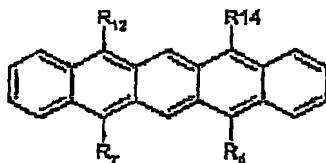
Formula 5

Compound Group 6 is represented by formula 6:



Formula 6

Compound Group 7 is represented by formula 7:



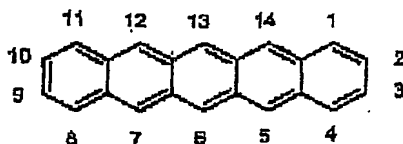
Formula 7

and wherein, in the case of Compound Group 1  $R_6$  and  $R_{13}$ , in the case of Compound Group 2  $R_6$  and  $R_{14}$ , in the case of Compound Group 3  $R_2$ ,  $R_3$ ,  $R_9$  and  $R_{10}$ , in the case of Compound Group 4  $R_2$  and  $R_{13}$ , in the case of Compound Group 5  $R_2$ ,  $R_3$ ,  $R_{11}$  and  $R_{12}$ , in the case of Compound Group 6  $R_2$  and  $R_9$ , and in the case of Compound Group 7  $R_3$ ,  $R_7$ ,  $R_{12}$  and  $R_{14}$  each independently represents an optionally substituted  $C_1$ - $C_{40}$  carbonyl or hydrocarbonyl group; an optionally substituted  $C_1$ - $C_{40}$  alkoxy group; an optionally substituted  $C_3$ - $C_{40}$  aryloxy group; an optionally substituted  $C_7$ - $C_{40}$  alkylaryloxy group; an optionally substituted  $C_2$ - $C_{40}$  alkoxycarbonyl group; an optionally substituted  $C_7$ - $C_{40}$  aryloxycarbonyl group; a cyano group ( $-CN$ ); a carbamoyl group ( $-C(=O)NH_2$ ); a haloformyl group ( $-C(=O)-X$ ); wherein  $X$  represents a halogen atom; a formyl group ( $-C(=O)-H$ ); an isocyanato group;



an isocyanate group; a thiocyanate group or a thioisocyanate group; an optionally substituted amino group; a hydroxy group; a halo group; or an optionally substituted silyl group; wherein each pair of  $R_2$  and  $R_3$  and/or  $R_8$  and  $R_{10}$  may be cross-bridged with each other to form a  $C_4$ - $C_{40}$  saturated or unsaturated ring, which saturated or unsaturated ring may be intervened by an oxygen atom, a sulphur atom or a group shown by formula:  $-N(R_9)-$  (wherein  $R_9$  is a hydrogen atom or a hydrocarbon group), or may optionally be substituted.

The "R" substituents (i.e.  $R_1$ ,  $R_2$  etc) in Compound Groups 1-7 denote the substituents at the positions of pentacene according to conventional nomenclature:



Surprisingly and beneficially, the inventors of the present invention have found that combining the specified soluble polyacene compounds, especially the pentacene compounds from Compound Groups 1-7, (hereinafter often referred to as "the polyacene") with an organic binder resin (hereinafter sometimes simply called a "binder") results in little or no reduction in charge mobility of the polyacene, even an increase in some instances. For instance, the soluble polyacene may be dissolved in a binder resin (e.g. polystyrene) and deposited (e.g. by spin coating), to form an organic semiconducting layer yielding a high charge mobility, e.g.  $0.3 \text{ cm}^2/\text{Vs}$ . This result is particularly unexpected given that the prior art teaches that for such high mobilities a polyacene derivative compound is expected to require strong molecular ordering. Dilution in a binder would be expected to yield an order of magnitude reduction in mobility. We have found that even at 1:1 ratio of binder:polyacene the mobility is about the same as that of the pure polyacene compound. The result produced by the present invention is therefore surprising for both a) maintaining the mobility despite potential disruption of molecular order, and b) maintaining mobility despite the expected increase of intermolecular distance. It is particularly surprising that the size of crystalline grains is reduced upon using a binder yet the mobility is high. At the same time, a semiconducting layer formed therefrom exhibits excellent film forming characteristics and is particularly stable.

Once a formulation of high mobility is obtained by combining the polyacene with the binder, the resulting formulation leads to several other advantages. Since the polyacenes are soluble they may be deposited in a liquid form, e.g. from solution. With the additional use of the binder we have found that the formulation may be coated on a large area in a highly uniform manner. Without the use of binders the polyacene cannot be spin coated on large areas as it does not result in uniform films. In the prior art, spin and drop-casting of a pure polyacene layer may in some cases result in relatively high

mobility but it is difficult to provide a film with a constant mobility over the entire substrate. Second, it is possible to control the properties of the formulation to adjust to printing processes, e.g. viscosity, solid content, surface tension. It is also anticipated that the binder fills in volume between crystalline grains otherwise being void, making the organic semiconducting layer less sensitive to air and moisture. For example, layers formed according to the present invention show very good stability in OFET devices in air.

The invention also provides an organic semiconducting layer which comprises the organic semiconducting layer formulation.

The invention further provides a process for preparing the organic semiconducting layer which comprises (i) depositing on a substrate a liquid layer of a mixture which comprises the polyacene compound, the organic binder resin or precursor thereof and optionally a solvent, and (ii) forming from the liquid layer a solid layer which is the organic semiconducting layer. The process is described in more detail below.

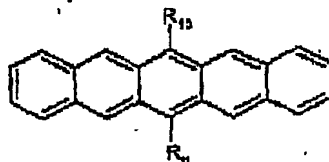
The invention additionally provides an electronic device comprising the said organic semiconducting layer. The electronic device may include, without limitation, an organic field effect transistor (OFET), organic light emitting diode (OLED), photodetector, sensor, logic circuit, memory element, capacitor or photovoltaic (PV) cell. For example, the active semiconductor channel between the drain and source in an OFET may comprise the layer of the invention. As another example, a charge (hole or electron) injection or transport layer in an OLED device may comprise the layer of the invention. The organic semiconducting layer may also find use forming at least part of an organic photoconductor (OPC) in an electrophotographic device. The formulation of the present invention and layers formed therefrom have particular utility in OFETs.

Certain polyacene compounds have been described in US 2003/0116755 A and US 6,690,029 and the methods disclosed therein for synthesising the polyacenes may be employed in the present invention in order to make the polyacene compounds. Methods for making the polyacenes are also described in US 3,557,233 (American Cyanamid). Alternatively, other methods within the skill and knowledge of persons skilled in the art may be used to synthesise the compounds.

The Compound Groups 1-7 are described in more detail now.

#### Compound Group 1

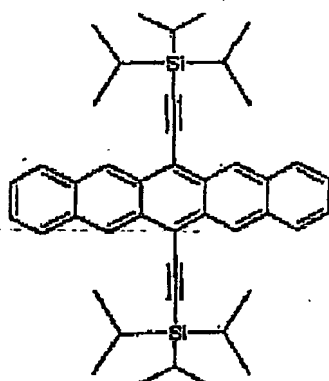
Compound Group 1 is represented by formula 1:



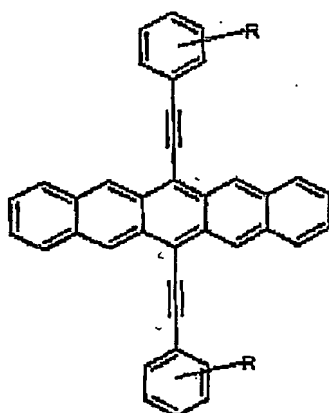
Formula 1

In pentacene derivatives of Compound Group 1,  $R_6$  and  $R_{13}$  are preferably the same substituent as each other. Preferably, the groups  $R_6$  and  $R_{13}$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. More preferably, the groups  $R_6$  and  $R_{13}$  comprise optionally substituted unsaturated  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups, e.g. optionally substituted alkenyl, alkynyl, aryl etc. groups (optionally substituted alkynyl is a preferred group, especially optionally substituted  $C_2$  ethynyl). Preferably, the  $R_6$  and  $R_{13}$  substituents are  $\pi$ -conjugated with the pentacene ring structure. In pentacene derivatives of Compound Group 1 one or more of the ring positions on the pentacene other than the 6 and 13 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

Examples of Compound Group 1 compounds are given below:



Group 1, example 1



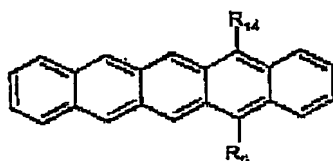
Group 1, example 2

An example of a compound of Compound Group 1 in which some of the remaining positions other than the 6,13 positions are also substituted is given below (wherein  $R_{16-17}$  are defined below):

Group 1, example 3

### Compound Group 2

Compound Group 2 is represented by formula 2:

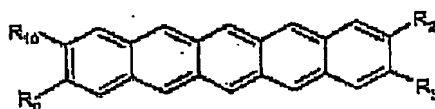


### Formula 2

In pentacene derivatives of Compound Group 2,  $R_8$  and  $R_{14}$  are preferably the same substituent as each other. Preferably, the groups  $R_8$  and  $R_{14}$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. More preferably, the groups  $R_8$  and  $R_{14}$  comprise optionally substituted unsaturated  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups, e.g. optionally substituted alkenyl, alkynyl, aryl etc. groups (optionally substituted alkynyl is a preferred group, especially optionally substituted  $C_2$  ethynyl). Preferably, the  $R_8$  and  $R_{14}$  substituents are  $\pi$ -conjugated with the pentacene ring structure. In pentacene derivatives of Compound Group 2 one or more of the ring positions on the pentacene other than the 5 and 14 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

### Compound Group 3

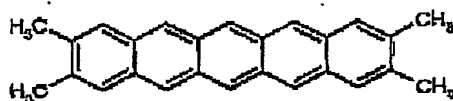
Compound Group 3 is represented by formula 3:



### Formula 3

In pentacene derivatives of group 3,  $R_2$  and  $R_3$  are preferably the same substituent as each other, and  $R_6$  and  $R_{10}$  are preferably the same substituent as each other. Preferably,  $R_2$ ,  $R_3$ ,  $R_6$  and  $R_{10}$  are the same substituent as each other. Preferably, the groups  $R_2$ ,  $R_3$ ,  $R_6$  and  $R_{10}$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. Further preferably, the groups  $R_2$ ,  $R_3$ ,  $R_6$  and  $R_{10}$  comprise optionally substituted  $C_1$ - $C_{10}$  carbyl or hydrocarbyl groups (especially alkyl), e.g. methyl, ethyl, propyl, butyl, pentyl, etc. One or more of the ring positions on the pentacene other than the 2, 3, 9 and 10 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

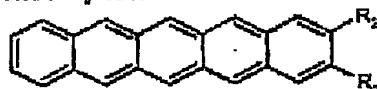
An example of a Compound Group 3 compound is given below:



Group 3, example

#### Compound Group 4

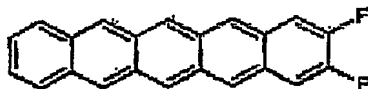
Compound Group 4 is represented by formula 4:



Formula 4

In pentacene derivatives of Compound Group 4,  $R_2$  and  $R_3$  are preferably the same substituent as each other. Preferably, the groups  $R_2$  and  $R_3$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups or halo. In pentacene derivatives of Compound Group 4, one or more of the ring positions on the pentacene other than the 2 and 3 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

An example of a Compound Group 4 compound is given below:

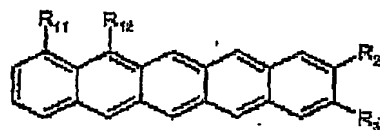


Group 4 example

#### Compound Group 5

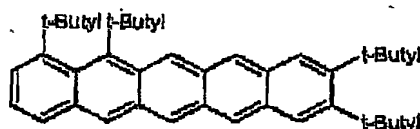
Compound Group 5 is represented by formula 5:

10



Formula 5

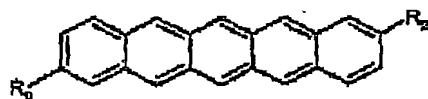
In pentacene derivatives of Compound Group 4,  $R_{11}$  and  $R_{12}$  are preferably the same substituent as each other, and  $R_2$  and  $R_3$  are preferably the same substituent as each other. Preferably,  $R_2$ ,  $R_3$ ,  $R_{11}$  and  $R_{12}$  are the same substituent as each other. Preferably, the groups  $R_2$ ,  $R_3$ ,  $R_{11}$  and  $R_{12}$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. Further preferably, the groups  $R_2$ ,  $R_3$ ,  $R_{11}$  and  $R_{12}$  comprise optionally substituted  $C_1$ - $C_{10}$  carbyl or hydrocarbyl groups, e.g. methyl, ethyl, propyl, butyl, pentyl, etc. In pentacene derivatives of Compound Group 5, one or more of the ring positions on the pentacene other than the 2, 3, 11 and 12 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen. An example of a Compound Group 5 compound is given below:



Group 5, example

### Compound Group 6

Compound Group 6 is represented by formula 6:

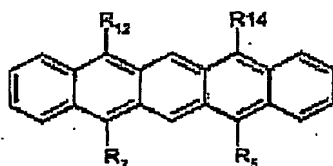


Formula 6

In pentacene derivatives of Compound Group 6,  $R_2$  and  $R_1$  are preferably the same substituent as each other. Preferably, the groups  $R_2$  and  $R_1$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. In pentacene derivatives of Compound Group 6, one or more of the ring positions on the pentacene other than the 2 and 9 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

Compound Group 7

Compound Group 7 is represented by formula 7:



Formula 7

In pentacene derivatives of Compound Group 7,  $R_5$  and  $R_{14}$  are preferably the same substituent as each other.  $R_7$  and  $R_{12}$  are preferably the same substituent as each other. Preferably,  $R_5$ ,  $R_{14}$ ,  $R_7$  and  $R_{12}$  are all the same substituent as each other. Preferably, the groups  $R_5$ ,  $R_{14}$ ,  $R_7$  and  $R_{12}$  comprise optionally substituted  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups. In pentacene derivatives of Compound Group 7, one or more of the ring positions on the pentacene other than the 5, 14, 7 and 12 positions may be substituted but preferably they are unsubstituted, i.e. they are occupied by hydrogen.

Preferably, the "R" groups ( $R_1$ ,  $R_2$  etc.) in Compound Groups 1-7 are  $C_1$ - $C_{40}$  carbyl or hydrocarbyl which may optionally be substituted. Preferably the optional substituent comprises silyl as herein defined below.

In the polyacenes of the present invention (especially Compound Groups 1-7), the  $C_1$ - $C_{40}$  carbyl or hydrocarbyl group may be a saturated or unsaturated acyclic group, or a saturated or unsaturated cyclic group. Unsaturated acyclic or cyclic groups are preferred, especially alkenyl and alkynyl groups (especially ethynyl). Where the  $C_1$ - $C_{40}$  carbyl or hydrocarbyl group is acyclic, the group may be linear or branched. The  $C_1$ - $C_{40}$  carbyl or hydrocarbyl group includes a  $C_1$ - $C_{40}$  alkyl group, a  $C_2$ - $C_{40}$  alkenyl group, a  $C_2$ - $C_{40}$  alkynyl group, a  $C_3$ - $C_{40}$  allyl group, a  $C_4$ - $C_{40}$  alkyldienyl group, a  $C_4$ - $C_{40}$  polyenyl group, a  $C_6$ - $C_{16}$  aryl group, a  $C_6$ - $C_{40}$  alkylaryl group, a  $C_6$ - $C_{40}$  arylalkyl group, a  $C_4$ - $C_{40}$  cycloalkyl group, a  $C_4$ - $C_{40}$  cycloalkenyl group, and the like. Preferred among the foregoing groups are a  $C_1$ - $C_{20}$  alkyl group, a  $C_2$ - $C_{20}$  alkenyl group, a  $C_2$ - $C_{20}$  alkynyl group, a  $C_3$ - $C_{20}$  allyl group, a  $C_4$ - $C_{20}$  alkyldienyl group, a  $C_6$ - $C_{12}$  aryl group and a  $C_4$ - $C_{20}$  polyenyl group, respectively; more preferred are a  $C_1$ - $C_{10}$  alkyl group, a  $C_2$ - $C_{10}$  alkenyl group, a  $C_2$ - $C_{10}$  alkynyl group (especially ethynyl), a  $C_3$ - $C_{10}$  allyl group, a  $C_4$ - $C_{10}$  alkyldienyl group, a  $C_6$ - $C_{12}$  aryl group and a  $C_4$ - $C_{10}$  polyenyl group, respectively; and most preferred is  $C_{2-10}$  alkynyl.

Examples of the alkyl group are, without limitation, methyl, ethyl, propyl, n-butyl, t-butyl, dodecanyl, trifluoromethyl, perfluoro-n-butyl, 2,2,2-trifluoroethyl, benzyl, 2-phenoxyethyl, etc. Examples of the alkynyl group are ethynyl and propynyl. Examples of the aryl group are, without limitation, phenyl, 2-tolyl, 3-tolyl, 4-tolyl, naphthyl, biphenyl, 4-phenoxyphenyl, 4-fluorophenyl, 3-carbomethoxyphenyl, 4-carbomethoxyphenyl, etc.

Examples of the alkoxy group are, without limitation, methoxy, ethoxy, 2-methoxyethoxy, t-butoxy, etc. Examples of the aryloxy group are, without limitation, phenoxy, naphthoxy, phenylphenoxy, 4-methylphenoxy, etc. Examples of the amino group are, without limitation, dimethylamino, methylamino, methylphenylamino, phenylamino, etc.

In the polyacenes of the present invention, the optional substituents on the said  $C_1$ - $C_{40}$  carbyl or hydrocarbyl groups for  $R_1$ , etc. preferably are selected from: silyl, sulphy, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halo,  $C_1$ - $C_{40}$  alkyl,  $C_6$ - $C_{40}$  aryl,  $C_1$ - $C_{40}$  alkoxy, hydroxy and/or all chemically possible combinations thereof. More preferable among these optional substituents are silyl and  $C_6$ - $C_{40}$  aryl and most preferable is silyl.

The silyl group in this specification, which may be optionally substituted, may be shown by formula:  $-Si(R_{15})(R_{16})(R_{17})$ , wherein each of  $R_{15}$ ,  $R_{16}$  and  $R_{17}$ , which may be the same or different, independently represents hydrogen, a  $C_1$ - $C_{40}$  alkyl group (preferably  $C_1$ - $C_4$  alkyl and most preferably methyl, ethyl, n-propyl or isopropyl) which may optionally be substituted e.g. with a halogen atom; a  $C_6$ - $C_{40}$  aryl group (preferably phenyl) which may optionally be substituted e.g. with a halogen atom; a  $C_6$ - $C_{40}$  arylalkyl group which may optionally be substituted e.g. with a halogen atom; a  $C_1$ - $C_{40}$  alkoxy group which may optionally be substituted e.g. with a halogen atom; or a  $C_6$ - $C_{40}$  arylalkoxy group which may optionally be substituted e.g. with a halogen atom. Preferably,  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  are each independently selected from optionally substituted  $C_1$ - $C_{10}$  alkyl (more preferably  $C_1$ - $C_3$  and even more preferably  $C_1$ - $C_3$  alkyl, e.g. isopropyl) and optionally substituted  $C_6$ - $C_{10}$  aryl (preferably phenyl).

In one preferred embodiment of silyl group,  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  are preferably the same group as each other, e.g. the same optionally substituted alkyl group, as in triisopropylsilyl. Preferably, in that preferred embodiment, the groups  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  are the same optionally substituted  $C_1$ - $C_{10}$  (more preferably  $C_1$ - $C_3$  and even more preferably  $C_1$ - $C_3$ ) alkyl group. A preferred alkyl group in this case is isopropyl.

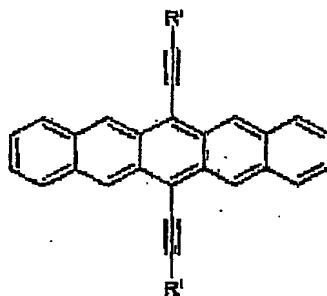
A silyl group of formula  $-Si(R_{15})(R_{16})(R_{17})$  as described above is a preferred optional substituent for the  $C_1$ - $C_{40}$  carbyl or hydrocarbyl group etc.

Examples of the silyl group  $-Si(R_{15})(R_{16})(R_{17})$  are, without limitation, trimethylsilyl, triethylsilyl, tripropylsilyl, dimethylethylsilyl, diethylmethylsilyl, dimethylpropylsilyl, dimethylisopropylsilyl, dipropylmethylsilyl, diisopropylmethylsilyl, dipropylethylsilyl, diisopropylethylsilyl, diethylisopropylsilyl, triisopropylsilyl, trimethoxysilyl, triethoxysilyl, triphenylsilyl, diphenylisopropylsilyl, diisopropylphenylsilyl, diphenylethylsilyl, diethylphenylsilyl, diphenylmethylsilyl, triphenoxysilyl, dimethylmethoxysilyl, dimethylphenoxysilyl, methylmethoxyphenyl, etc. For each example in the foregoing list, the alkyl, aryl or alkoxy group may optionally be substituted.

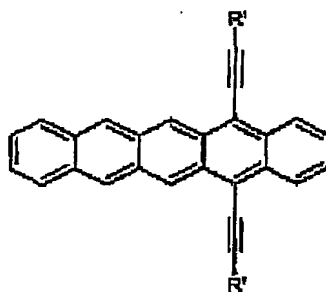
Most preferred pentacene compounds of the invention are those of Compound Groups 1 and 2 (especially Compound Group 1). More preferred among Compound Groups 1 and 2 are compounds of formula 1A or 2A (especially formula 1A):



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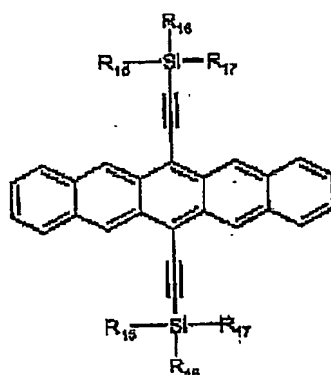
Formula 1A



Formula 2A

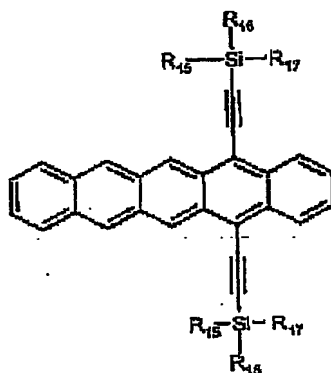
wherein each R' is independently selected from a C<sub>2-40</sub> alkyl group, a C<sub>2-40</sub> alkoxy group, a C<sub>2-40</sub> alkenyl group, C<sub>2-40</sub> alkynyl group, a C<sub>6-16</sub> aryl or heteroaryl group, C<sub>6</sub>-C<sub>40</sub> aryloxy group, C<sub>7</sub>-C<sub>40</sub> alkylaryloxy group, a C<sub>2</sub>-C<sub>40</sub> alkoxycarbonyl group, a C<sub>7</sub>-C<sub>40</sub> aryloxycarbonyl group, or a silyl group, each of which may be optionally substituted, or a cyano group (-CN), a carbamoyl group (-C(=O)NH<sub>2</sub>), a haloformyl group (-C(=O)-X wherein X represents a halogen atom), a formyl group (-C(=O)-H), an isocyano group, an isocyanate group, a thiocyanate group or a thioisocyanate group, an optionally substituted amino group, an imino group, a hydroxy group, a halo, a sulpho group, a sulphonyl group a mercapto group, or a nitro group. Preferably, in formulae 1A and 2A, each R' is independently selected from C<sub>6-16</sub> aryl and silyl, which may both optionally be substituted. Preferably in formula 1A or 2A, at least one R' and most preferably both R' is silyl, wherein the silyl group is preferably defined as above, i.e. a silyl group of formula -Si(R<sub>16</sub>)(R<sub>16</sub>)(R<sub>17</sub>). These latter highly preferred compounds thus have formulae 1B and 2B:

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Formula 1B

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Formula 2B

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Examples of compounds of formulae 1B and 2B include, without limitation:

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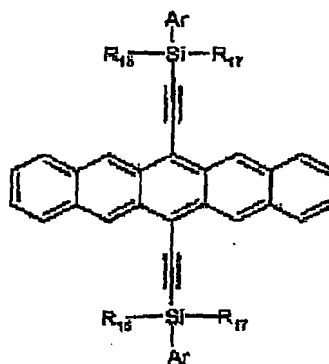
- 6,13-bis(trimethylsilylethynyl)pentacene
- 6,13-bis(triethylsilylethynyl)pentacene
- 6,13-bis(tripropylsilylethynyl)pentacene
- 6,13-bis(dimethylethylsilylethynyl)pentacene
- 6,13-bis(dielethylmethylsilylethynyl)pentacene
- 6,13-bis(dimethylpropylsilylethynyl)pentacene
- 6,13-bis(dimethylisopropylsilylethynyl)pentacene
- 6,13-bis(dipropylmethylsilylethynyl)pentacene
- 6,13-bis(diisopropylmethylsilylethynyl)pentacene
- 6,13-bis(dipropylethylsilylethynyl)pentacene
- 6,13-bis(dilisopropylethylsilylethynyl)pentacene
- 6,13-bis(diethylisopropylsilylethynyl)pentacene
- 6,13-bis(trisopropylsilylethynyl)pentacene
- 6,13-bis(trimethoxysilylethynyl)pentacene

- 6,13-bis(triethoxysilylethynyl)pentacene
- 6,13-bis(triphenylsilylethynyl)pentacene
- 6,13-bis(diphenylisopropylsilylethynyl)pentacene
- 6,13-bis(diisopropylphenylsilylethynyl)pentacene
- 5 6,13-bis(diphenylethylsilylethynyl)pentacene
- 6,13-bis(diethylphenylsilylethynyl)pentacene
- 6,13-bis(diphenylmethylsilylethynyl)pentacene
- 6,13-bis(triphenoxysilylethynyl)pentacene
- 6,13-bis(dimethylmethoxysilylethynyl)pentacene
- 10 6,13-bis(dimethylphenoxysilylethynyl)pentacene
- 6,13-bis(methylmethoxyphenylethynyl)pentacene
- 5,14-bis(trimethylsilylethynyl)pentacene
- 5,14-bis(triethylsilylethynyl)pentacene
- 5,14-bis(tripropylsilylethynyl)pentacene
- 15 5,14-bis(dimethylethylsilylethynyl)pentacene
- 5,14-bis(diethylmethylsilylethynyl)pentacene
- 5,14-bis(dimethylpropylsilylethynyl)pentacene
- 5,14-bis(dimethylisopropylsilylethynyl)pentacene
- 5,14-bis(dipropylmethylsilylethynyl)pentacene
- 20 5,14-bis(diisopropylmethylsilylethynyl)pentacene
- 5,14-bis(dipropylethylsilylethynyl)pentacene
- 5,14-bis(diisopropylethylsilylethynyl)pentacene
- 5,14-bis(dlethylisopropylsilylethynyl)pentacene
- 5,14-bis(trisopropylsilylethynyl)pentacene
- 25 5,14-bis(trimethoxysilylethynyl)pentacene
- 5,14-bis(triethoxysilylethynyl)pentacene
- 5,14-bis(triphenylsilylethynyl)pentacene
- 5,14-bis(diphenylisopropylsilylethynyl)pentacene
- 5,14-bis(diisopropylphenylsilylethynyl)pentacene
- 30 5,14-bis(diphenylethylsilylethynyl)pentacene
- 5,14-bis(dlethylphenylsilylethynyl)pentacene
- 5,14-bis(diphenylmethylsilylethynyl)pentacene
- 5,14-bis(triphenoxysilylethynyl)pentacene
- 5,14-bis(dimethylmethoxysilylethynyl)pentacene
- 35 5,14-bis(dimethylphenoxysilylethynyl)pentacene
- 5,14-bis(methylmethoxyphenylethynyl)pentacene

In one type of preferred embodiment,  $R_{16}$ ,  $R_{18}$  and  $R_{17}$  in formulae 1B and 2B are preferably the same as each other, e.g. the same alkyl group, as in the preferred

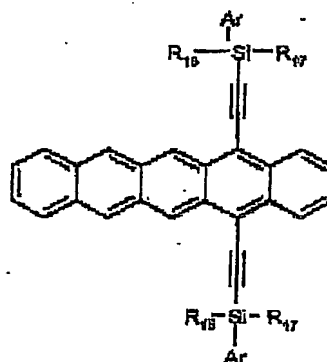
examples of 6,13-bis-(trisopropylsilylethynyl)pentacene and 5,14-bis-(trisopropylsilylethynyl)pentacene. In this particular preferred embodiment,  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  are preferably the same  $C_{1-10}$  (preferably  $C_{1-4}$  and more preferably  $C_{1-3}$ ) alkyl group which may optionally be substituted. Optionally substituted isopropyl is a preferred alkyl group for such embodiments.

In some cases it may be desirable to control the solubility of the polyacene in common organic solvents in order to make devices easier to fabricate. This may have advantages in making an FET for example, where solution coating, say, a dielectric onto the polyacene layer may have a tendency to dissolve the polyacene. Also, once a device is formed, a less soluble polyacene may have less tendency to "bleed" across organic layers. In one preferred embodiment, in order to control solubility of the pentacene derivatives of formulae 1B and 2B above, at least one of  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  contains an optionally substituted aryl (preferably phenyl) group. Thus, at least one of  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  may be an optionally substituted  $C_{6-18}$  aryl (preferably phenyl) group; an optionally substituted  $C_{6-18}$  aryloxy (preferably phenoxy) group, an optionally substituted  $C_{6-20}$  arylalkyl (e.g. benzyl) group, or an optionally substituted  $C_{6-20}$  arylalkyloxy (e.g. benzyloxy) group. In such cases, the remaining groups, if any, among  $R_{15}$ ,  $R_{16}$  and  $R_{17}$  are preferably  $C_{1-10}$  (more preferably  $C_{1-4}$ ) alkyl groups which may be optionally substituted. Examples of such preferred embodiments of compounds are given below with formulae 1C and 2C, wherein Ar represents an aryl-containing group e.g. an optionally substituted  $C_{6-18}$  aryl group, an optionally substituted  $C_{6-18}$  aryloxy group, an optionally substituted  $C_{6-20}$  arylalkyl group or an optionally substituted  $C_{6-20}$  arylalkyloxy group.



Formula 1C

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Formula 2C

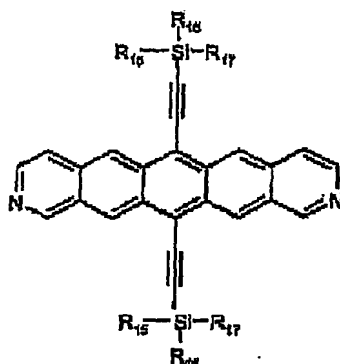
In the formulae 1C and 2C,  $R_{16}$  and  $R_{17}$  are preferably the same group as each other, e.g. an isopropyl group. Compounds of formulae 1C and 2C are believed to be novel and are claimed per se. Additionally, many of the other substituted polyacene compounds disclosed in this specification for use in the present invention are also believed to be novel and, as such, are also claimed per se.

Examples of compounds of Formulae 1C and 2C include, without limitation:

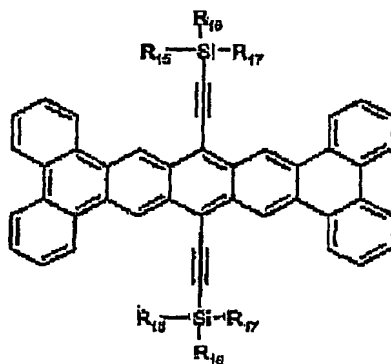
- 6,13-bis(triphenylsilylethynyl)pentacene
- 6,13-bis(diphenylisopropylsilylethynyl)pentacene
- 6,13-bis(diisopropylphenylsilylethynyl)pentacene
- 6,13-bis(diphenylethylsilylethynyl)pentacene
- 6,13-bis(diethylphenylsilylethynyl)pentacene
- 6,13-bis(diphenylmethylsilylethynyl)pentacene
- 6,13-bis(triphenoxysilylethynyl)pentacene
- 6,13-bis(dimethylphenoxysilylethynyl)pentacene
- 6,13-bis(methylmethoxyphenylethynyl)pentacene
- 5,14-bis(triphenylsilylethynyl)pentacene
- 5,14-bis(diphenylisopropylsilylethynyl)pentacene
- 5,14-bis(diisopropylphenylsilylethynyl)pentacene
- 5,14-bis(diphenylethylsilylethynyl)pentacene
- 5,14-bis(diethylphenylsilylethynyl)pentacene
- 5,14-bis(diphenylmethylsilylethynyl)pentacene
- 5,14-bis(triphenoxysilylethynyl)pentacene
- 5,14-bis(dimethylphenoxysilylethynyl)pentacene
- 5,14-bis(methylmethoxyphenylethynyl)pentacene

In one embodiment, one or more of the carbon atoms of the polyacene skeleton

may be substituted by a heteroatom selected from N, P, As, O, S, Se and Te, preferably N. An example of such a compound, wherein two of the carbon atoms of the pentacene skeleton have been substituted by N, is given below:



In one embodiment, any two or more of the substituents  $R_1$ - $R_{12}$  which are located on adjacent ring positions of the polyacene may, together, optionally constitute a further aromatic ring system fused to the polyacene. An example is given below wherein each pair of adjacent substituents  $R_1$  and  $R_2$ ;  $R_3$  and  $R_4$ ;  $R_5$  and  $R_6$ ; and  $R_{10}$  and  $R_{11}$  constitute a benzene ring fused to the pentacene:



In a preferred embodiment the semiconducting polyacene has a field effect mobility,  $\mu$ , of more than  $10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , preferably of more than  $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , more preferably of more than  $10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , still more preferably of more than  $10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and most preferably of more than  $10^{-1} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

The organic binder resin, which is a polymer, may be referred to herein as the organic binder or simply the binder.

Preferred binders are materials of low permittivity, i.e. those having a permittivity,  $\epsilon$ , at 1,000 Hz of 3.3 or less. However, binders of higher permittivity may be used. The organic binder preferably has a permittivity at 1,000 Hz of less than 3.0, more preferably

2.8, or less. Preferably the organic binder has a permittivity at 1,000 Hz greater than 1.7, especially a permittivity from 2.0 to 2.8.

An example of a suitable organic binder is polystyrene. Further examples are given below.

5 In one type of preferred embodiment, the organic binder is one in which at least 95%, more preferably at least 98% and especially all of the atoms consist of hydrogen, fluorine and carbon atoms.

It is preferred that the binder normally contains conjugated bonds especially conjugated double bonds and/or aromatic rings.

10 The binder should preferably be capable of forming a film, more preferably a flexible film. Copolymers of styrene and alpha methyl styrene, for example copolymers of styrene, alpha methyl styrene and butadiene may suitably be used.

Binders of low permittivity of use in the present invention have few permanent dipoles which could otherwise lead to random fluctuations in molecular site energies. The permittivity (dielectric constant) can be determined by the ASTM D150 test method.

15 It is desirable that the permittivity of the binder has little dependence on frequency. This is typical of non-polar materials. Polymers and/or copolymers can be chosen as the binder by the permittivity of their substituent groups. A list of low polarity binders suitable for use in the present invention is given (without limiting to these examples) in Table 1 :

Table 1

Binder	typical low frequency permittivity $\epsilon$
polystyrene	2.5
poly( $\alpha$ -methylstyrene)	2.6
poly( $\alpha$ -vinyl naphthalene)	2.6
poly(vinyltoluene)	2.6
polyethylene	2.2-2.3
cis-polybutadiene	2.0
polypropylene	2.2
polyisoprene	2.3
poly(4-methyl-1-pentene)	2.1
poly(tetrafluoroethylene)	2.1
poly(chlorotrifluoroethylene)	2.3-2.8
poly(2-methyl-1,3-butadiene)	2.4
poly(p-xylylene)	2.6
poly( $\alpha$ - $\beta$ - $\alpha'$ - $\alpha'$ tetrafluoro-p-xylylene)	2.4
poly[1,1-(2-methyl propane)bis(4-phenyl)carbonate]	2.3
poly(cyclohexyl methacrylate)	2.6
poly(chlorostyrene)	2.6
poly(2,6-dimethyl-1,4-phenylene ether)	2.6
polyisobutylene	2.2
poly(vinyl cyclohexane)	2.2

Other polymers suitable as binders include poly(4-methylstyrene), poly(1,3-butadiene) or polyphenylene. Copolymers containing the repeat units of the above polymers are also suitable as binders. Copolymers offer the possibility of improving compatibility with the polyacene, modifying the morphology and/or the glass transition temperature of the final layer composition. It will be appreciated that in the above table certain materials are insoluble in commonly used solvents for preparing the layer. In these cases analogues can be used as copolymers. Some examples of copolymers are given in Table 2 (without limiting to these examples). Both random or block copolymers can be used. It is also possible to add some more polar monomer components as long as the overall composition remains low in polarity.



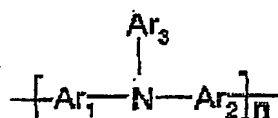
Table 2

Binder	typical low frequency permittivity ( $\epsilon$ )
poly(ethylene/tetrafluoroethylene)	2.6
poly(ethylene/chlorotrifluoroethylene)	2.3
fluorinated ethylene/propylene copolymer	2-2.5
polystyrene-co- $\alpha$ -methylstyrene	2.5-2.6
ethylene/ethyl acrylate copolymer	2.8
poly(styrene/10%butadiene)	2.6
poly(styrene/15%butadiene)	2.6
poly(styrene/2,4 dimethylstyrene)	2.5

Other copolymers may include branched or non-branched polystyrene-block-polybutadiene, polystyrene-block(polyethylene-ran-butylene)-block-polystyrene, polystyrene-block-polybutadiene-block-polystyrene, polystyrene-(ethylene-propylene)-diblock-copolymers (e.g. KRATON® G1701E, Shell), poly(propylene-co-ethylene) and poly(styrene-co-methylmethacrylate).

The organic binder itself may be a semiconductor, where it will be referred to herein as a semiconducting binder. The semiconducting binder is still preferably a binder of low permittivity as herein defined. The semiconducting binder preferably has a number average molecular weight ( $M_n$ ) of at least 2000, more preferably at least 3000, even more preferably at least 4000 and most preferably at least 5000. The semiconducting binder preferably has a charge carrier mobility,  $\mu$ , of at least  $10^{-5} \text{ cm}^2/\text{V.s}$ , more preferably at least  $10^{-4} \text{ cm}^2/\text{V.s}$ .

A preferred class of semiconducting binder has repeat units of a formula 8



Formula 8

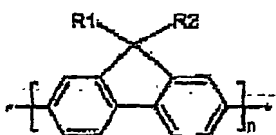
wherein  $\text{Ar}^1$ ,  $\text{Ar}^2$  and  $\text{Ar}^3$ , which may be the same or different, each represent, independently if in different repeat units, an optionally substituted aromatic group (mononuclear or polynuclear) and in the resin  $n$  is an integer of at least 5, preferably at least 10, more preferably at least 15 and most preferably at least 20. In the context of  $\text{Ar}^1$ ,  $\text{Ar}^2$  and  $\text{Ar}^3$ , a mononuclear aromatic group has only one aromatic ring, for example phenyl or phenylene. A polynuclear aromatic group has two or more aromatic rings which

may be fused (for example naphthyl or naphthylene), individually covalently linked (for example biphenyl) and/or a combination of both fused and individually linked aromatic rings. Preferably each  $Ar^1$ ,  $Ar^2$  and  $Ar^3$  is an aromatic group which is substantially conjugated over substantially the whole group.

5 Preferred classes of semiconducting binders are those containing substantially conjugated repeat units. The semiconducting polymer may be a homopolymer or copolymer (including a block-copolymer) of the general formula 9:

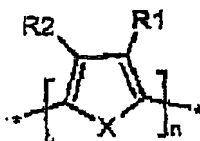


10 Where A, B,...,Z each represent a monomer unit and (c), (d),...(z) each represent the fraction of the respective monomer unit in the polymer, i.e. each (c), (d),...(z) is a value from 0 to 1 and the total of (c) + (d) +...+ (z) = 1. Examples of monomer units A, B,...,Z include units of formula 8 and formulae 10-15 given below.



Formula 10

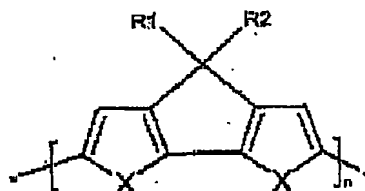
15 where R1 and R2 may be independently H; optionally substituted alkyl; alkoxy; thioalkyl; acyl; optionally substituted aryl; a fluorine atom; a cyano group; a nitro group; an optionally substituted secondary or tertiary alkylamine or arylamine  $-N(R_a)(R_b)$ , where  $R_a$  and  $R_b$  may each be independently represented by H, alkyl, substituted alkyl, aryl, substituted aryl, alkoxy or polyalkoxy groups; or other substituent and - is any terminal or end capping group including hydrogen (the alkyl and aryl groups may be optionally fluorinated);



Formula 11

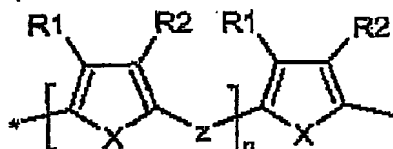
25 in which X may be Se, Te or preferably O, S or  $-N(R)-$ , where R represents H, alkyl, substituted alkyl, aryl, or substituted aryl; R1 and R2 are as for formula 10;

23



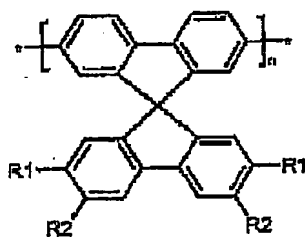
Formula 12

In which X is as for formula 11, and R1 and R2 are as for formula 10;



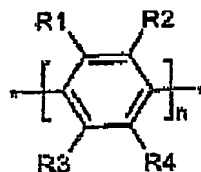
Formula 13

In which X is as for formula 11; R1, R2 are as for formula 10; and Z represents -C(T<sub>1</sub>)=C(T<sub>2</sub>)-, -C≡C-, -N(R')-, -N=N-, (R')=N-, -N=C(R')-, T<sub>1</sub> and T<sub>2</sub> independently represent -H, Cl, F, -C≡N or a lower alkyl, R' represents -H, alkyl, substituted alkyl, aryl, or substituted aryl;



Formula 14

where R1 and R2 are as for formula 10;



Formula 15

where R1-R4 may be independently selected from the same list of groups as for R1 and R2 in formula 10.

In the case of polymeric formulae herein, such as formulae 8-15, the polymers may be terminated by any terminal group, i.e. any end-capping or leaving group, including hydrogen.

In the case of a block-copolymer, each monomer A, B,...Z may be a conjugated oligomer or polymer comprising a number, for example 2 to 50, of the units of formulae 10-15. The semiconducting binder preferably includes arylamine, fluorene, thiophene, spiro bifluorene and/or optionally substituted aryl (e.g. phenylene) groups, more preferably arylamine, still more preferably triarylamine. The aforementioned groups may be linked by further conjugating groups e.g. vinylene. Additionally preferably the semiconducting binder comprises a polymer (either a homo-polymer or copolymer, including block-copolymer) containing one or more of the aforementioned arylamine, fluorene, thiophene and/or optionally substituted aryl groups. A preferred semiconducting binder comprises a homo-polymer or copolymer (including block-copolymer) containing arylamine (preferably triarylamine) and/or fluorene units. Another preferred semiconducting binder comprises a homo-polymer or co-polymer (including block-copolymer) containing fluorene and/or thiophene units.

The semiconducting binder may also contain carbazole, stilbene repeat units. For example polyvinylcarbazole or polystilbene polymers, copolymers may be used. The semiconducting binder may optionally contain polyacene segments (e.g. repeat units as formula A above) to improve compatibility with the soluble polyacene molecules.

For application of the semiconducting layer of the invention in p-channel FETs, it is desirable that the binder should have a higher ionisation potential than the polyacene semiconductor, otherwise the binder may form hole traps. In n-channel materials the binder should have lower electron affinity than the n-type semiconductor to avoid electron trapping.

The formulation according to the invention may be prepared by a process which comprises first mixing both the polyacene compound and the organic binder, preferably the mixing comprises mixing the two components together in a solvent or solvent mixture. The solvent may be a single solvent or the polyacene compound and the organic binder may each be dissolved in a separate solvent followed by mixing the two resultant solutions to mix the compounds. The solvent(s) containing the polyacene compound and the organic binder may then be applied to a substrate. The solvent(s) may be evaporated to form the layer of the invention.

The binder may be formed *in situ* by mixing or dissolving the polyacene in a precursor of the binder, for example a liquid monomer, oligomer or crosslinkable polymer, optionally in the presence of a solvent, and depositing the mixture or solution, for example

by dipping, spraying, painting or printing it, on a substrate to form a liquid layer and then curing the liquid monomer, oligomer or crosslinkable polymer, for example by exposure to radiation, heat or electron beams, to produce a solid layer.

If a preformed binder is used it may be dissolved together with the polyacene in a suitable solvent, and the solution deposited for example by dipping, spraying, painting or printing it on a substrate to form a liquid layer and then removing the solvent to leave a solid layer. Suitable solvents are chosen from those classes which are a good solvent for both the binder and polyacene, and which upon evaporation from the solution blend give a coherent defect free layer. Suitable solvents for the binder or polyacene can be determined by preparing a contour diagram for the material as described in ASTM Method D 3132 at the concentration at which the mixture will be employed. The material is added to a wide variety of solvents as described in the ASTM method. Examples of organic solvents which may be considered are:  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , monochlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, n-butyl acetate, dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetralin, decalin and/or mixtures thereof. After the appropriate mixing and ageing, solutions are evaluated as one of the following categories: complete solution, borderline solution or insoluble. The contour line is drawn to outline the solubility parameter-hydrogen bonding limits dividing solubility and insolubility. 'Complete' solvents falling within the solubility area can be chosen from literature values such as published in "Crowley, J.D., Teague, G.S. Jr and Lowe, J.W. Jr., Journal of Paint Technology, 38, No 496, 296 (1966)". Solvent blends may also be used and can be identified as described in "Solvents, W.H.Ellis, Federation of Societies for Coatings Technology, pg-10, 1986". Such a procedure may lead to a blend of 'non' solvents that will dissolve both the binder and polyacene, although it is desirable to have at least one true solvent in a blend.

The proportions of the binder to the polyacene in the formulation or layer according to the present invention are typically 20:1 to 1:20, preferably 10:1 to 1:10 more preferably 5:1 to 1:5, still more preferably 3:1 to 1:3 and most preferably 2:1 to 1:2 (e.g. about 1:1). Surprisingly and beneficially, dilution of the polyacene in the binder has been found to have little or no effect on the charge mobility, in contrast to what would have been expected from the prior art.

It is desirable to generate small structures in modern microelectronics to reduce cost (more devices/unit area), and power consumption. Patterning of the layer of the invention may be carried out by photolithography or electron beam lithography.

Liquid coating of organic electronic devices such as field effect transistors is more desirable than vacuum deposition techniques. The polyacene and binder mixtures of the present invention enable the use of a number of liquid coating techniques. The organic

semiconductor layer may be incorporated into the final device structure by, for example and without limitation, dip coating, spin coating, ink jet printing, letter-press printing, screen printing, doctor blade coating; roller printing, reverse-roller printing; offset lithography printing, flexographic printing, web printing, spray coating, brush coating or pad printing.

Selected polyacene and binder compositions of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

In order to be applied by ink jet printing or microdispensing, polyacene and binder compositions must first be dissolved in a suitable solvent. Solvents must fulfil the requirements stated above and must not have any detrimental effect on the chosen print head. Additionally, solvents should have boiling points  $>100^{\circ}\text{C}$ , preferably  $>140^{\circ}\text{C}$  and more preferably  $>150^{\circ}\text{C}$  in order to prevent operability problems caused by the solution drying out inside the print head. Suitable solvents include substituted and non-substituted xylene derivatives, di- $\text{C}_{1-2}$ -alkyl formamide, substituted and non-substituted anisoles and other phenol-ether derivatives, substituted heterocycles such as substituted pyridines, pyrazines, pyrimidines, pyrrolidinones, substituted and non-substituted  $\text{N,N-di-C}_{1-2}$ -alkylanilines and other fluorinated or chlorinated aromatics.

A preferred solvent for depositing the binder/polyacene formulation by ink jet printing comprises a benzene derivative which has a benzene ring substituted by one or more substituents wherein the total number of carbon atoms among the one or more substituents is at least three. For example, the benzene derivative may be substituted with a propyl group or three methyl groups, in either case there being at least three carbon atoms in total. Such a solvent enables an ink jet fluid to be formed comprising the solvent with the binder and polyacene which reduces or prevents clogging of the jets and separation of the components during spraying. The solvent(s) may include those selected from the following list of examples: dodecylbenzene; 1-Methyl-4-tert-butylbenzene; Terpineol; Limonene; Isodurene; Terpinolene; Cymene; Diethylbenzene. The solvent may be a solvent mixture, i.e. a combination of two or more solvents, each solvent preferably having a boiling point  $>100^{\circ}\text{C}$ , more preferably  $>140^{\circ}\text{C}$ . Such solvent(s) also enhance film formation in the layer deposited and reduce defects in the layer.

The ink jet fluid (i.e. mixture of solvent, binder and polyacene) preferably has a viscosity at  $20^{\circ}\text{C}$  of 1-100mPa.s, more preferably 1-50mPa.s and most preferably 1-30mPa.s

The use of the binder in the present invention also allows the viscosity of the coating solution to be tuned to meet the requirements of the particular print head.

The semiconducting layer of the present invention is typically at most 1 micron (=1 $\mu$ m) thick, although it may be thicker if required. The exact thickness of the layer will depend, for example, upon the requirements of the electronic device in which the layer is used. For use in an OFET or OLED, the layer thickness may typically be 500 nm or less.

In the semiconducting layer of the present invention there may be used two or more different polyacene compounds of formula 1. Additionally or alternatively, in the semiconducting layer there may be used two or more organic binder resins of the present invention.

As mentioned above, the invention further provides a process for preparing the organic semiconducting layer which comprises (i) depositing on a substrate a liquid layer of a mixture which comprises the polyacene compound, the organic binder resin or precursor thereof and optionally a solvent, and (ii) forming from the liquid layer a solid layer which is the organic semiconducting layer.

In the process, the solid layer may be formed by evaporation of the solvent and/or by reacting the binder resin precursor (if present) to form the binder resin *in situ*. The substrate may include any underlying device layer, electrode or separate substrate such as silicon wafer or polymer substrate for example.

In one particular embodiment of the present invention, the binder may be alignable, e.g. capable of forming a liquid crystalline phase. In that case the binder may assist alignment of the polyacene, e.g. such that the polyacene backbone is preferentially aligned along the direction of charge transport. Suitable processes for aligning the binder include those processes used to align polymeric organic semiconductors such as described in WO 03/007397 (Plastic Logic).

The present invention also provides the use of the semiconducting formulation or layer in an electronic device. The formulation may be used as a high mobility semiconducting material in various devices and apparatus. The formulation may be used, for example, in the form of a semiconducting layer or film. Accordingly, in another aspect, the present invention provides a semiconducting layer for use in an electronic device, the layer comprising the formulation according to the invention. The layer or film may be less than about thirty microns. For various electronic device applications, the thickness may be less than about one micron thick. The layer may be deposited, e.g. on a part of an electronic device, by any of the aforementioned solution coating or printing techniques.

The formulation may be used, e.g. as a layer or film, in a field effect transistor (FET) e.g. as the semiconducting channel, organic light emitting diode (OLED) e.g. as a hole or electron injection or transport layer or electroluminescent layer, photodetector, chemical detector, photovoltaic cell (PVs), capacitor sensor, logic circuit, display, memory device and the like. The formulation may also be used in electrophotographic

(EP) apparatus, e.g. in the organic photoconductor. The formulation is preferably solution coated to form a layer or film in the aforementioned devices or apparatus to provide advantages in cost and versatility of manufacture. The improved charge carrier mobility of the formulation of the present invention enables such devices or apparatus to operate faster and/or more efficiently. The formulation and layer of the present invention are especially suitable for use in an OFET as the semiconducting channel. Accordingly, the invention also provides an organic field effect transistor (OFET) comprising a source electrode, a drain electrode and an organic semiconducting channel connecting the source and drain electrodes, wherein the organic semiconducting channel comprises a layer according to the present invention. Other features of the OFET are well known to those skilled in the art.

Some definitions and explanations of terms used herein are now given.

When in the formulae herein there is a list of labels (e.g.  $R_1$ ,  $R_2$  etc.) or indices (e.g. 'n') which are said to represent a list of groups or numerical values, and these are said to be "independent in each case" this indicates each label and/or index can represent any of those groups listed independently from each other, independently within each repeat unit, independently within each Formula and/or independently on each group which is substituted as appropriate. Thus, in each of these instances, many different groups might be represented by a single label (e.g.  $R_5$ ).

The terms 'substituent', 'substituted', 'optional substituent' and/or 'optionally substituted' as used herein (unless followed by a list of other substituents) signifies at least one of the following groups (or substitution by these groups): silyl, sulphy, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halo,  $C_{1-4}$ alkyl,  $C_{6-12}$  aryl,  $C_{1-4}$ alkoxy, hydroxy and/or combinations thereof. These optional groups may comprise all chemically possible combinations in the same group and/or a plurality (preferably two) of the aforementioned groups (e.g. amino and sulphonyl if directly attached to each other represent a sulphamoyl radical). Preferred optional substituents comprise:  $C_{1-4}$ alkyl; methoxy and/or ethoxy (any of these optionally substituted by at least one halo); amino (optionally substituted by at least one methyl and/or ethyl); and/or halo.

The term 'carbonyl group' as used herein denotes any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either without any non-carbon atoms (e.g.  $-C\equiv C-$ ), or optionally combined with at least one other non-carbon atom (e.g. alkoxy, carbonyl etc.).

The term 'hydrocarbon group', 'hydrocarbyl' or the like may be used herein interchangeably. A hydrocarbon group may be optionally substituted. A hydrocarbon group may also contain at least one of the following heteroatom containing moieties: oxy, thio, sulphy, sulphonyl, amino, imino, nitrilo and/or combinations thereof.

The terms 'alkyl', 'aryl', etc. as used herein may be readily replaced, where appropriate, by terms denoting a different degree of valence e.g. multivalent species (e.g.



alkylene, arylene, etc.).

The term 'halo' as used herein signifies fluoro, chloro, bromo and iodo.

Unless the context clearly indicates otherwise, a group herein which comprises a chain of three or more carbon atoms signifies a group in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings).

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

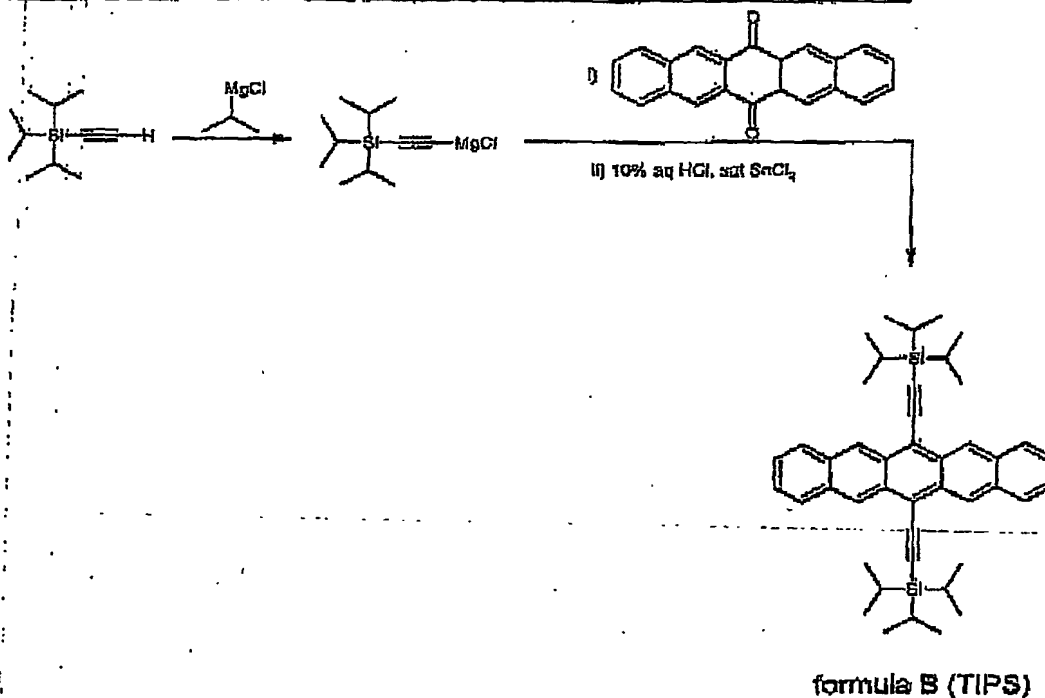
Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components.

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

The invention will now be described in more detail by reference to the following examples, which are illustrative only and do not limit the scope of the invention.

Examples.Synthesis of semiconductorsSynthesis of 6, 13-bis(trisopropylsilyl)ethynylpentacene - formula B (TIPS)

To a flame-dried flask fitted with mechanical stirrer, nitrogen inlet and outlet, condenser and suba-seal was added isopropylmagnesium chloride (2M in THF (10 molar equivalents based on 6, 13-pentacenequinone)). This solution was cooled using a cold-water bath to act as a cold trap to absorb any exotherm during the trisopropylsilyl acetylene addition. Trisopropylsilyl acetylene (10.1 molar equivalents based on 6, 13-pentacenequinone) was added to the reaction flask drop-wise over 30 minutes followed by the addition of THF (10ml for every 10mmol of TIPS acetylene). The cold-water bath was removed and then this solution was heated at 60 °C for 20 minutes. The flask was then allowed to cool to room temperature. 6, 13-Pentacenequinone (1 molar equivalent) was added to the Grignard reagent and the resulting cloudy suspension was heated at 60 °C until the reaction was deemed complete according to HPLC, this may take up to 3 hours. The flask was allowed to cool to room temperature. A solution of 10% aqueous HCl saturated with tin (II) chloride was added cautiously to the brown / red reaction solution until the solution no longer exothermed on addition. (It is noted that as the tin (II) chloride solution was added, the reaction solution turned from brown / red to a deep blue colour). The resulting solution was heated at 60 °C for 30 minutes before cooling to room temperature.

This crude mixture was worked up using water / DCM drying the organic phase over  $\text{MgSO}_4$ , before filtering and concentrating under vacuum to give a blue / black solid. Purification by column chromatography (silica gel, 5% DCM in hexane) followed by recrystallisation from acetone yielded the title compound as dark blue plates.

#### Determination of the Field Effect Mobility

The field effect mobility of the materials was tested using the techniques described by Holland et al, J. Appl. Phys. Vol.75, p.7954 (1994).

In the following examples a test field effect transistor was manufactured by using a PEN substrate upon which were patterned Pt/Pd source and drain electrodes by standard techniques, e.g. shadow masking. Semiconductor formulations were made using TIPS (formula B above) blended with an inert binder resin (poly(alpha-methylstyrene)). The semiconductor formulation was dissolved one part into 99 parts of toluene, and spin coated onto the substrate at 500 rpm for 18s. To ensure complete drying the sample was placed in an oven for 20 minutes at 100 °C. For comparison films of purely TIPS material were coated by spin coating. These were then dried in an oven for 20 min at 100 °C. The insulator material (Cytop 107M, Asahi glass) was mixed 3 parts to 2 parts of perfluorosolvent (FC75, Acros cat. no. 12380) and then spin-coated onto the semiconductor giving a thickness typically of approximately 1  $\mu\text{m}$ . The sample was placed once more in an oven at 100 °C to evaporate solvent from the insulator. A gold gate contact was defined over the device channel area by evaporation through a shadow mask. To determine the capacitance of the insulator layer a number of devices were prepared which consisted of a non-patterned Pt/Pd base layer, an insulator layer prepared in the same way as that on the FET device, and a top electrode of known geometry. The capacitance was measured using a hand-held multimeter, connected to the metal either side of the insulator. Other defining parameters of the transistor are the length of the drain and source electrodes facing each other ( $W=30 \text{ mm}$ ) and their distance from each other ( $L=130 \mu\text{m}$ ).

The voltages applied to the transistor are relative to the potential of the source electrode. In the case of a p type gate material, when a negative potential is applied to the gate, positive charge carriers (holes) are accumulated in the semiconductor on the other side of the gate dielectric. (For an n channel FET, positive voltages are applied). This is called the accumulation mode. The capacitance/area of the gate dielectric  $C_g$  determines the amount of the charge thus induced. When a negative potential  $V_{gs}$  is applied to the gate, the accumulated carriers yield a source-drain current  $I_{ds}$  which depends primarily on the density of accumulated carriers and, importantly, their mobility in the source-drain channel. Geometric factors such as the drain and source electrode configuration, size and distance also affect the current. Typically a range of gate and drain voltages are scanned during the study of the device. The source-drain current is

described by equation 1.

$$I_{DS} = \frac{\mu WC_i}{L} \left( (V_G - V_0) V_{DS} - \frac{V_{DS}^2}{2} \right) + I_0, \quad \text{eq.1}$$

where  $V_0$  is an offset voltage and  $I_0$  is an ohmic current independent of the gate voltage and is due to the finite conductivity of the material. The other parameters have been described above.

For the electrical measurements the transistor sample was mounted in a sample holder. Microprobe connections were made to the gate, drain and source electrodes using Karl Suss PH100 miniature probe-heads. These were linked to a Hewlett-Packard 4155B parameter analyser. The drain voltage was set to -20 V and the gate voltage was scanned from +20 to -60V and back to +20V in 1 V steps. In accumulation, when  $|V_G| > |V_{DS}|$  the source-drain current varies linearly with  $V_G$ . Thus the field effect mobility can be calculated from the gradient ( $S$ ) of  $I_{DS}$  vs.  $V_G$  given by equation 2.

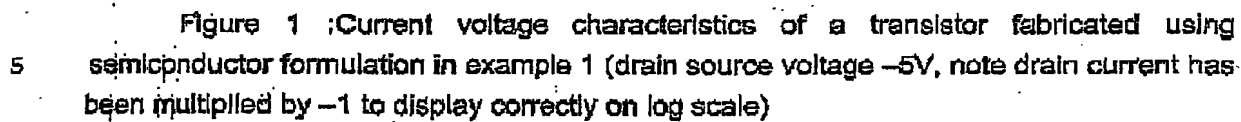
$$S = \frac{\mu WC_i V_{DS}}{L} \quad \text{eq. 2.}$$

All field effect mobilities quoted below were calculated from this regime (unless stated otherwise). Where the field effect mobility varied with gate voltage, the value was taken as the highest level reached in the regime where  $|V_G| > |V_{DS}|$  in accumulation mode. The values quoted in table 3 are an average taken over several devices (fabricated on the same substrate), the sample size is also quoted in Table 3. An example of the current-voltage and mobility-voltage characteristics for example 1 is shown in figure 1. The forward and reverse scans illustrate the low hysteresis of the device. The results show the excellent charge mobility obtained when the pentacene compound is combined with the binder resin at up to 50 % wt.

Table 3: results of the formulations tested

Example number	Organic semiconducting material (OSC)	Binder	OSC : binder ratio (wt:wt)	OSC coating method	Mobility [ $\text{cm}^2/\text{Vs}$ ]	Sample size
1	Formula B	p- $\alpha$ MS	50:50	Spin coat	0.433	9
2	Formula B	p- $\alpha$ MS	75:25	Spin coat	0.321	7
3	Formula B	p- $\alpha$ MS	90:10	Spin coat	0.327	6
4	Formula B	p- $\alpha$ MS	95:5	Spin coat	0.244	8
5 (comparative)	Formula B	-	100	Spin coat	0.138	6

p- $\alpha$ MS = Poly(alpha-methylstyrene), Aldrich Cat no. 19,184-1.



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